Improvement of Erosion Resistance of Titanium with Different Surface Treatments

Yongqing Fu, Hejun Du, and Yanwei Gu

(Submitted 11 November 1999)

To improve the erosion resistance of titanium, several surface treatment methods were applied: (1) duplex treatment with carbon nitride film deposited on a plasma-nitrided layer, (2) diamond coating, and (3) laser alloying. Duplex treatment could improve the erosion resistance of titanium under a low impact velocity of erosion particles. However, under a high velocity of erosion particles, because of the shallow depth of the plasma-nitrided layer and low load-bearing capacity of carbon nitride layer on the plasma-nitrided specimen, the improvement of erosion resistance was not significant. Diamond coatings with a thickness of 15 μm made no significant improvement on the erosion resistance of the titanium substrate. The large-area spallation of diamond coating during erosion was observed, probably due to the high residual stresses, poor load-bearing capacity, and brittle nature of diamond coatings. Compared with untreated Ti substrate, the erosion resistance of the laser-alloyed (nitrided) specimen was improved significantly. The erosion mechanisms for laser-nitrided titanium were characterized by chipping, brittle fracture, and formation of large flakes in the laser-nitrided layers.

Keywords diamond coatings, erosion/wear, plasma nitriding, surface modification, titanium

1. Introduction

Aircraft, rockets, and other aeronautical engines are often subjected to severe erosion situations from sands, rains, or other solid particles in space. Erosion by these solid particles or raindrop impingement can cause rapid degradation of mechanical properties and even catastrophic failure. Examples of the failure components include the blades and discs of aircraft compressors, helicopter rotor blades, valves and piping, *etc.*[1] Most of these components are made of titanium alloys, which are notorious for their poor erosion and wear resistance.[2] Different approaches have been put forward to solve this problem: (1) filtering the air entering the compressor, which is an efficient solution but limits the engine yield, (2) using stainless steel blades, which are approximately twice as resistant to Ti alloy blades but much heavier, and (3) protecting the blades by surface treatments and erosion-resistant coatings.

To design and use protective coatings or surface treatments that withstand solid particle erosion is thought to be the best approach to solve this problem. However, numerous factors, including the size, shape, hardness, flow rate, velocity, impingement angle of the erodents,[1,3] coating, and substrate materials properties (such as microstructure, hardness, tensile strength, residual stresses, ductility, fracture toughness, *etc.*[4,5]), have been reported to complicate the development of a successful protective coating. Several protective coating systems have been developed, for example, overlay deposition techniques such as thermal spraying and physical vapor deposition (PVD) techniques.[6,7] Researchers have also proposed and applied PVD or chemical vapor deposition (CVD) multilayer coatings (such as W/WC and W/W-N) with the appropriate stacking arrangement to improve the erosion resistance.[8,9,10]

Diamond coatings prepared by plasma-enhanced chemical vapor deposition (PECVD) or a hot-filament method have recently been studied to protect titanium substrate from erosion damage.[11,12,13] Diamond has the potential to be an excellent erosion-resistant material because of its high hardness, high wear resistance, and good thermal-shock resistance. It was reported that the most important parameter controlling the erosion resistance was the coating thickness.[11,14] With a sufficient thickness, the diamond coating outperformed the reference materials, whereas a too thin coating yielded poor erosion resistance. However, so far, most studies on the erosion of diamond coatings were performed under low particle velocities and small particle sizes.[15]

Plasma nitriding of titanium alloys has been considered as a good method to solve the wear and corrosion resistance of titanium alloys. However, few studies have been reported on the improvement of erosion resistance of titanium substrate using plasma nitriding. There are some studies on the duplex treatment combining plasma nitriding and CN_X films on Ti alloy substrate.[16] Plasma nitriding of Ti alloy produces a graded hardened case that serves as a supporting layer for the hard CN_X films. The hard and smooth CN_X films deposited at low temperature can produce a wear-resistant and low-friction coating without impairing the beneficial effects of pre-plasma-nitriding treatment. Therefore, the duplex treatment is a potential technique for improving the wear resistance of Ti alloy.[17]

Laser remelting the surface in the presence of interstitial elements such as carbon or nitrogen is also expected to be an efficient method to improve the erosion resistance of titanium and its alloys.[18,19] However, little research work has been done using these surface treatment methods to improve the erosion resistance of Ti substrate.

Yongqing Fu, Hejun Du, and **Yanwei Gu**, Nanyang Technological University, Micromachines Lab, School of Mechanical and Production Engineering, Singapore, 639798. Contact e-mail: myqfu@ntu.edu.sg.

In this study, three types of surface-treated systems, a duplex-treated (plasma nitriding/carbon nitride) coating system, diamond coatings, and laser-surface-alloyed coatings were prepared on titanium substrate, and their erosion resistances under two types of sand particle velocities were evaluated.

2. Experimental Procedures

2.1 Coating Preparation and Characterization

Pure titanium plates with a thickness of 3 mm were mechanically ground with sandpapers and polished with diamond pastes (6 to 1 μm), then ultrasonically cleaned by acetone before deposition. Plasma nitriding was carried out on Ti plates with a total power of 2 kW and a voltage of 1500 V. The treatment temperature was 800 °C and the duration was 9 h. CN_X films were deposited on plasma-nitrided Ti plates by an unbalanced magnetron sputtering system under a base pressure of 6×10^{-4} Pa. A high-purity (99.99%) planar graphite target was used in a pure (99.999%) nitrogen discharge at a gas pressure of 5 Pa and a constant gas flow rate of 40 sccm. The discharge current on the cathode was held at 1 A, with the substrate temperature below 200 °C and the negative substrate bias voltage of -300 V.

Deposition of diamond coating on pure titanium was carried out by a MPS4 microwave plasma-assisted diamond CVD system (Coaxial Power Systems Ltd., Eastbourne, United Kingdom).[20] The output frequency was 2.45 GHz and the microwave plasma power was 1 kW. The gas ratio of methane to hydrogen was 196:4 and the total gas pressure was 30 Torr. The processing duration was 15 h.

For laser alloying, a Nd-YAG laser was selected to carry out the treatment in nitrogen atmosphere and the laser beam was defocused with a diameter of 3 mm. Before the laser treatment, commercial Ni, Cr powders, with 70% Ni and 30% Cr, were plasma sprayed on titanium substrate with an average thickness of about 50 μm in order to decrease the cracking susceptibility and improve the hardening effect during laser treatment.[18] The laser parameters used in the present study are listed as follows: laser power, 300 W; traverse speed, 15 mm/s; nitrogen pressure, 0.4 MPa; pulse width, 4 ms; pulse rate, 10 s^{-1}; and overlapping ratio, 50%.

The brittleness and load-bearing capacity of different surface-treated layers were evaluated using a Rockwell (Matsuzawa Seiko Co., Ltd., Tokyo, Japan) hardness tester under a normal load of 588 N. With the Rockwell hardness tester, the load-bearing capacity of a film was judged from the radial and lateral cracks as well as spallation after the indentation using scanning electron microscopy (SEM). The residual stresses of diamond and laser-alloyed coating were determined by the conventional $\sin^2 \psi$-2θ method.

2.2 Erosion Tests

For solid-particle erosion testing, a standard sandblasting apparatus was used to impact the target specimens (with a dimension of 10×10 mm) with erodents at various velocities. The solid particles used in erosion tests were natural angular alumina sands with dimensions of 200 to 300 μm. The impingement angle of the particles on the surface was $90 \pm 2°$. The erodent was accelerated by compressed air with the particle impact velocities of 100 and 250 m/s. The nozzle-to-specimen distance was maintained at 50 cm. The erosion performance was measured by weighing the specimens to an accuracy of ± 0.01 mg before and after exposure to the erodent for different test durations, so that the evolution of the mass loss with erosion time could be determined. Each sample was ultrasonically cleaned in acetone and the weight was measured three times to obtain an average value. All the experiments were performed at ambient condition with a temperature of 25 °C and a relative humidity of 50%. The erosion morphologies of the coatings were examined by SEM to characterize the erosion mechanisms.

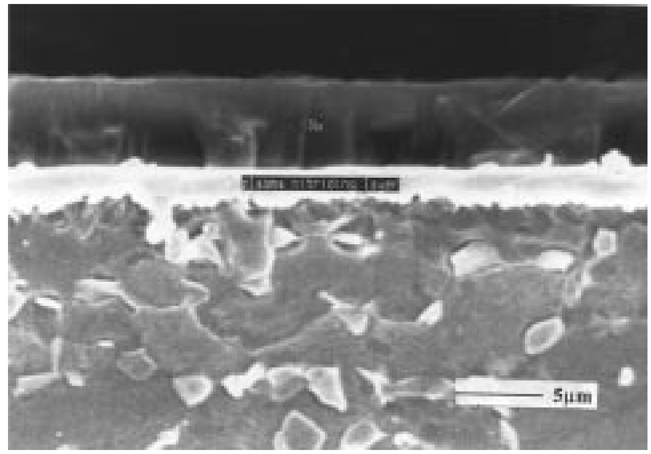


Fig. 1 Cross-sectional morphology of carbon nitride film deposited on plasma-nitrided Ti substrate

3. Results and Discussion

3.1 Characterization of Different Coating Systems

Figure 1 shows the cross-sectional morphology of a duplex-treated coating system. The CN_X film with a thickness of 5 μm is dense and free of porosity. There is no sign of cracking or debonding, and continuity is evident across the interfaces among Ti substrate, nitrided layer, and CN_X film, indicating a good adhesion between CN_X film and plasma-nitrided Ti substrate. Beneath the CN_X film is the plasma-nitrided layer, which is composed of two sublayers. The top sublayer (or the compound layer) consists of δ-TiN and ε-Ti_2N (up to about 1 to 2 μm thick).[21] The lower sublayer between the compound layer and titanium substrate contains a nitrogen-rich α-stabilized solid-solution-hardened zone (around 20 μm thick). The core material consists of retained β phase in a matrix of α-Ti. Transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, and x-ray photoelectron spectroscopy (XPS) analysis of CN_X films can be found in Ref 17 and 18. Figure 2 shows the indentation morphology of carbon nitride films deposited on plasma-nitrided specimen. There are some large radial cracks accomplished by a blister formation and slight debonding of CN_X films at the edge of the impression, indicating a relatively poor load-bearing capacity of CN_X films.

The SEM observation demonstrates that diamond coatings

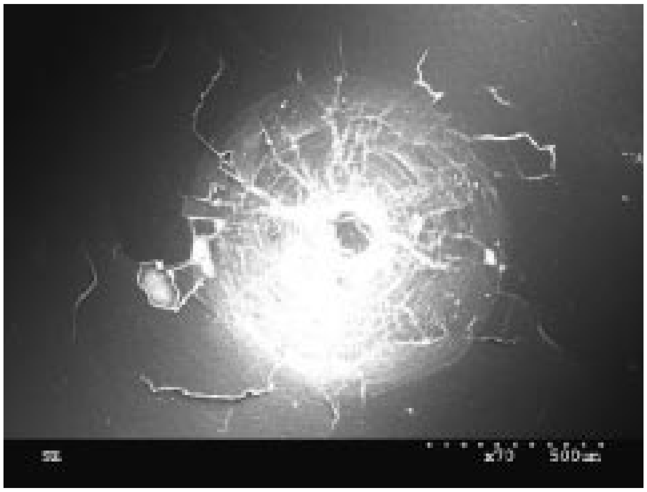


Fig. 2 The indentation morphology of CN_x film deposited on plasma-nitrided specimen showing the cracks and small-area spallation

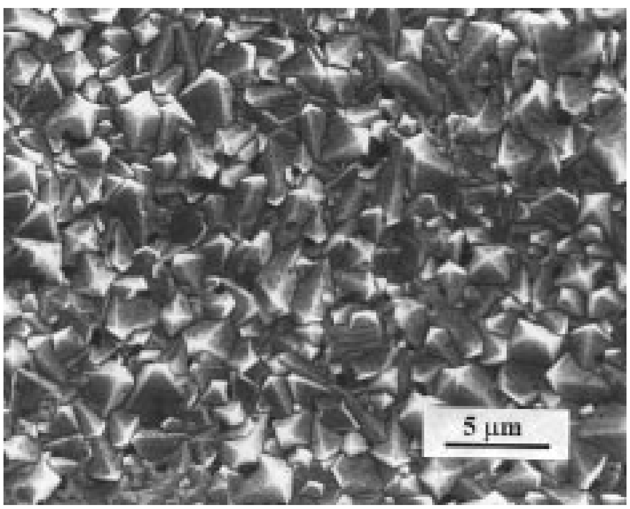


Fig. 3 The SEM observation of diamond coating showing the polycrystalline nature

are polycrystalline in nature with the crystal dimension of 2 to 4 μm (Fig. 3). The diamond coating is about 15 μm thick. The faceted surface morphology and the predominant (111) orientation are the typical characteristics of the deposited diamond coating.[20] The Raman spectra of diamond coating is shown in Fig. 4, which clearly demonstrates the presence of the characteristic diamond and diamond-like phases in the deposited coatings. The frequency shift of the diamond peak from the value of stress-free diamond at 1332 cm^{-1} indicates the existence of a residual compressive stress of approximately -5.12 GPa, calculated using the following equation:[23,24]

$$\sigma = -1.0 \times 10^{10} \, \Delta\nu, \text{ for } \{111\} \text{ crystals.} \quad \text{(Eq 1)}$$

Figure 5 shows the $\sin^2 \psi$-2θ curve obtained from the XRD stress analysis results of diamond coating. If we choose the elastic modulus of diamond as 800 GPa and Poisson ratio of 0.2, then the calculated residual stress is about -3.63 GPa, a datum that is near to that obtained by Raman analysis. Both

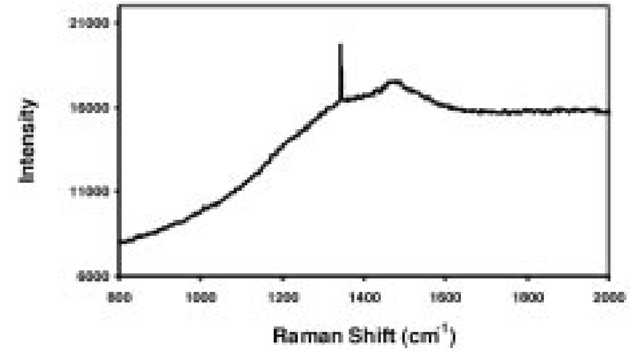


Fig. 4 Raman spectrum of diamond coatings showing the presence of the characteristic diamond and diamond-like phases in the deposited coatings

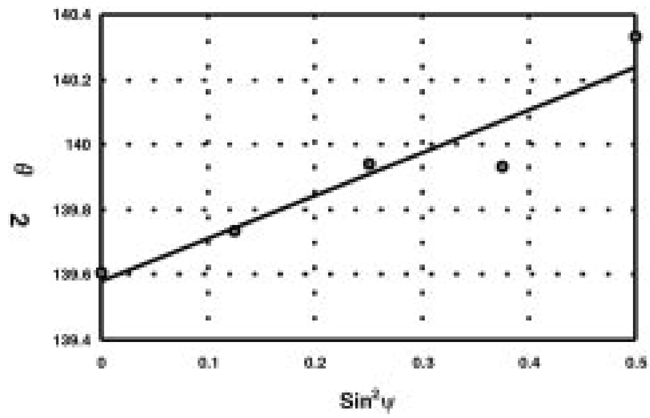


Fig. 5 The relationship of $\sin^2 \psi$ vs 2θ of diamond coating obtained from XRD results

Raman and XRD analysis show that an extremely large compressive stress exists in the deposited diamond coating. Figure 6 shows the indentation morphology of diamond coating. A large-area spallation of diamond coating is observed, indicating the poor adhesion strength of diamond coating on titanium substrate. This can be attributed to the brittle nature of diamond coatings and the existence of large residual stresses.

The detailed characterization of laser-alloyed titanium can be found in Ref 18. The maximum surface microhardness is over 1600 HV and the hardening depth is about 200 μm. The surface of the laser-treated specimen shows a highly reflective golden color, indicating the formation of near-stoichiometric TiN phases. The cross-sectional microstructure of the specimen is shown in Fig. 7. The near-surface microstructure is coarse and needlelike TiN dendrites. Beneath this layer is an acicular dendritic layer that is randomly distributed because the convection of liquid flow disturbs the dendrite growth of TiN phases. In the middle of the nitrided specimen, there is a layer that is composed of many randomly oriented fine dendrites and platelike structure and these are probably the mixture of TiN, α-Ti, and Ti_2N phases. Figure 8 shows the x-ray diffraction spectrum for the laser-treated specimens and the laser-nitrided layer is composed of TiN, Ti, and Ti_2N phases. Figure 9 shows the $\sin^2 \psi$-2θ curve obtained from the XRD stress analysis

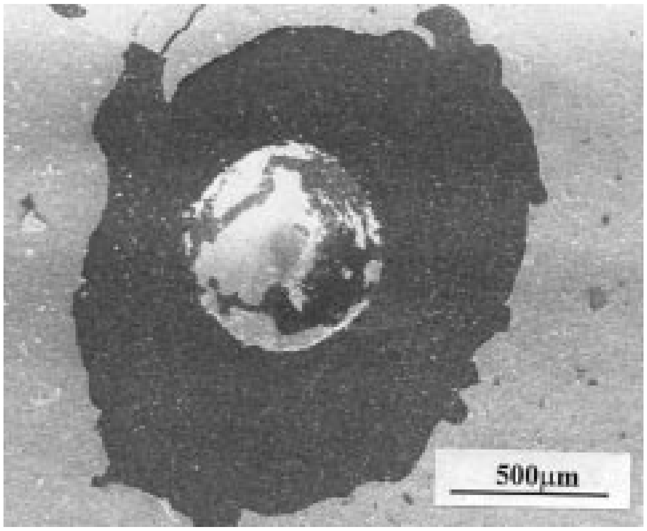


Fig. 6 Indentation morphology of diamond coating revealing the large-area spallation

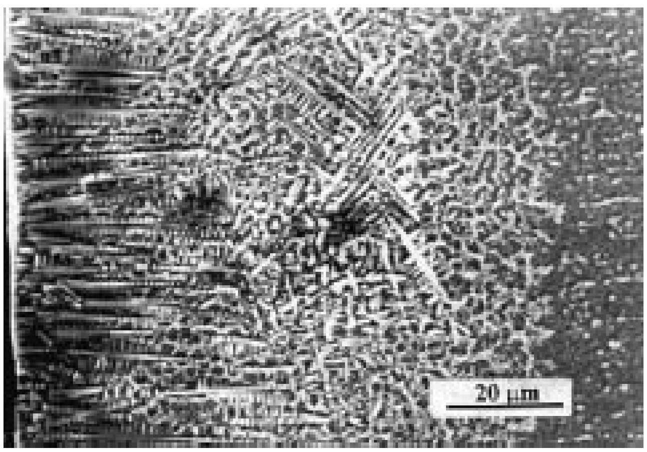


Fig. 7 Cross-sectional microstructure of a laser-alloyed titanium sample

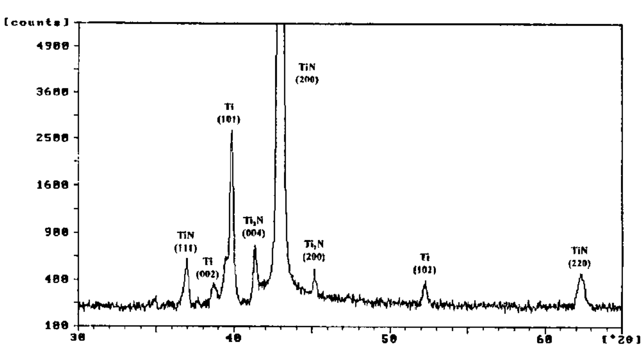


Fig. 8 XRD spectrum for the laser-alloyed specimen

results of laser-treated titanium. If we choose the elastic modulus of titanium nitride as 450 GPa and the Poisson ratio as 0.25, then the calculated residual stress in a laser-treated surface

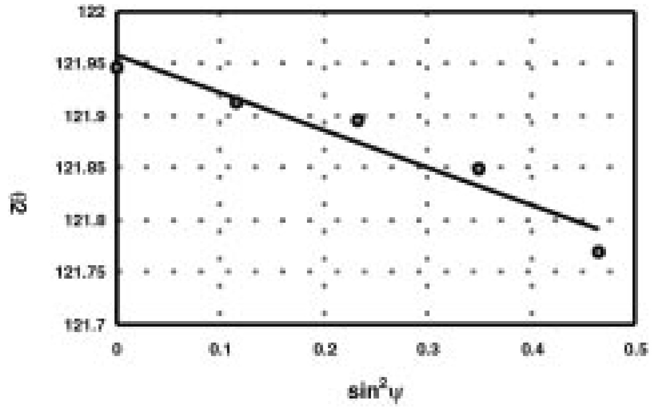


Fig. 9 The relationship of $\sin^2 \psi$ vs 2θ of laser-alloyed titanium obtained from XRD results

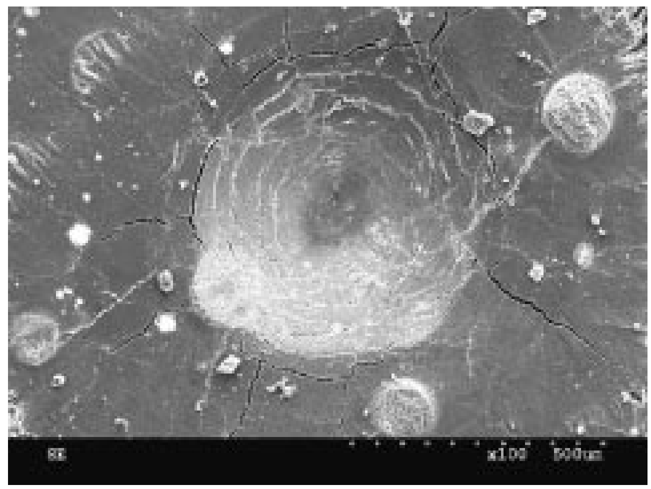
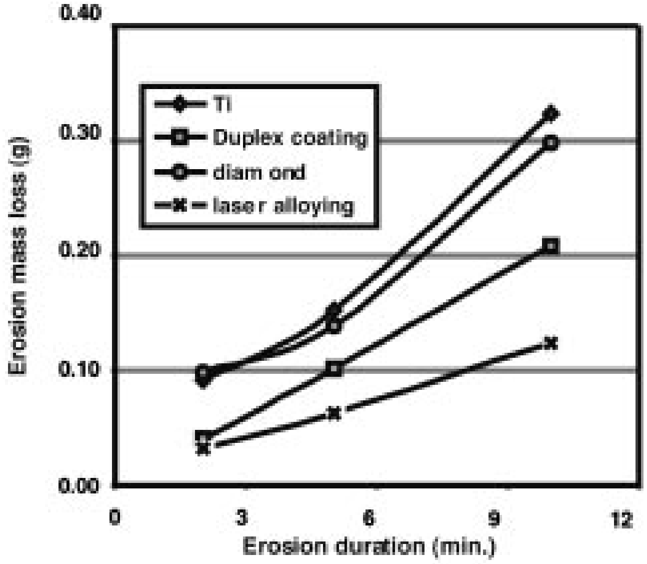


Fig. 10 Indentation morphology of the laser-alloyed titanium showing cracks and the brittle nature

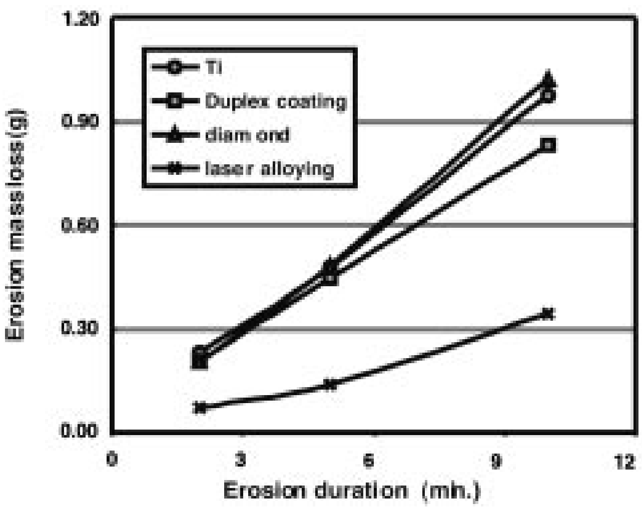
layer is about 516.3 MPa, tensile stress. Figure 10 shows the indentation morphology of the laser-alloyed titanium indicating its brittle nature. Some long radial cracks can be observed emanating from the indentation crater. This is due to the formation of hard titanium nitride phases and the tensile stress existing in the laser-alloyed coating.[24,25]

3.2 Erosion Behavior

3.2.1 Titanium Substrate. The mass loss of titanium substrate after exposure to an erodent is plotted as a function of the erosion duration in Fig. 11(a) and (b). Untreated titanium substrate displays a linear relation between the mass loss and erosion duration. For titanium substrate, degradation can rapidly occur through plastic deformation, microcutting, and particle indentation on the surface, as shown in Fig. 12(a) and (b). The accumulation of impacts with exposure time results in microcutting, ploughing, flake formation, overlapping of impact craters, and delamination of plastically deformed layers. The progressive work hardening increases the possibility of local fracture and leads to the detachment of thin platelets (Fig. 12c).

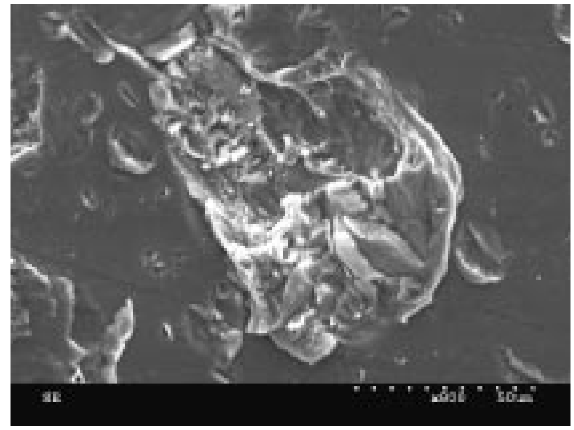


(**a**) impact velocity of 100 m/s

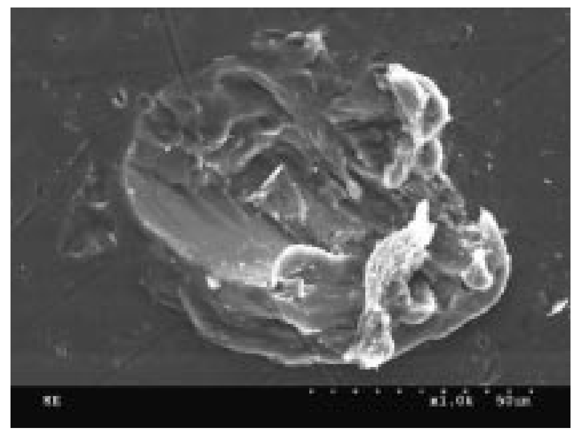


(**b**) impact velocity of 350 m/s

Fig. 11 The mass loss of titanium substrate, duplex-treated specimen, diamond-coated titanium, and laser-nitrided titanium substrate as a function of erosion duration under two different impact velocities; (**a**) impact velocity of 100 m/s and (**b**) impact velocity of 350 m/s



(**a**)



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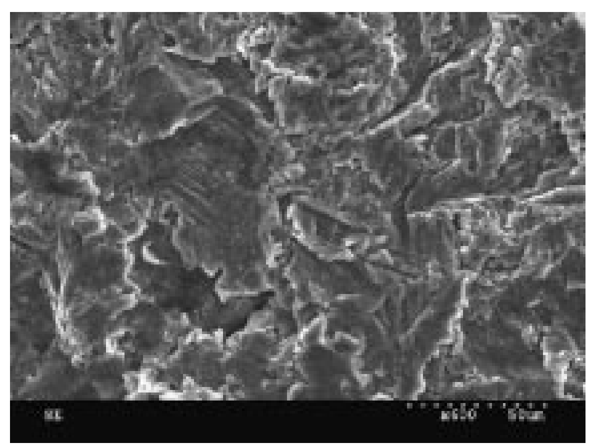


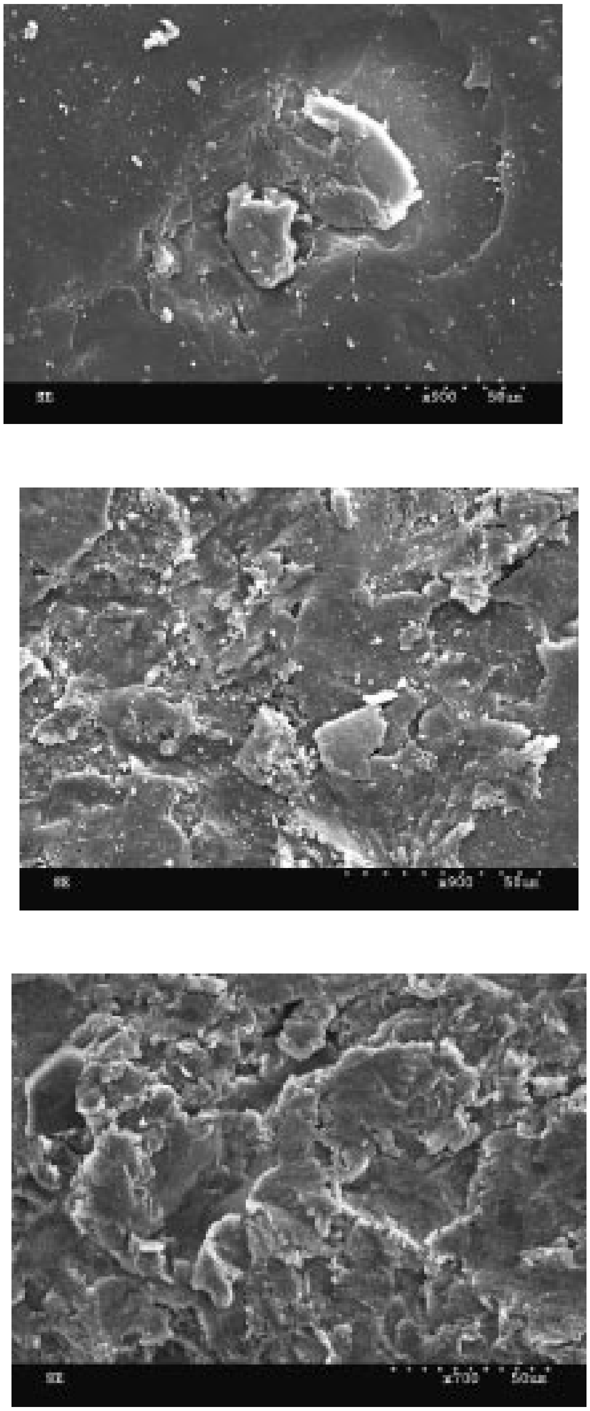
(**c**)

Fig. 12 (**a**) through (**c**) Erosion morphology of untreated pure Ti substrate

3.2.2 Duplex-Treated Coating. Figures 11(a) and (b) show the eroded mass losses of the duplex-treated system under different erosion conditions. The duplex-treated coating can improve the erosion resistance of titanium substrate under a low impact velocity because it contains a hardened layer, being able to resist the particle flux at low velocity. However, under a high velocity, due to the relatively low load-bearing capacity of CN_X film on a plasma-nitrided layer and shallow hardening depth of a plasma-nitrided layer, the improvement of erosion resistance is not so significant.

For carbon nitride coating deposited on a plasma-nitrided layer, when the erodent impacts on the coating surface, cracks form in the brittle carbon nitride layer. Then these cracks will grow parallel at the interface between the carbon nitride coating and the plasma-nitrided layer, and small parts of the films are torn out by impinging particles, as shown in Fig. 13(a). The predominant features of the eroded surface are microchipping, cracking, some degree of plastic deformation from direct impacts, and the detachment of thin platelets (Fig. 13b and c).

3.2.3 Diamond Coatings. Figure 11(a) and (b) show the mass loss of diamond-coated titanium samples during the ero



(**a**)

(**b**)

(**c**)

Fig. 13 (**a**) through (**c**) Erosion morphology of CN_x films deposited on plasma-nitrided titanium substrate

sion test. It can be observed that under both low and high velocities, the erosion mass losses of diamond-coated samples are almost the same as those of Ti substrate. Diamond-coated Ti samples show spalling as soon as the erosion test begins (Fig. 14a and b). During further erosion, stress-wave-induced debonding and delamination are the main erosion mechanisms for diamond coatings in our study, as shown in Fig. 14(c) and (d). The large-area spallation is due to the poor adhesion strength, large residual stresses, and brittle nature of diamond coatings on titanium substrate, and also due to the severe damage of the soft substrate, which causes the separation of the coating and substrate. The damage process for CVD diamond films by sand particle impact follows the following sequence: (1) rapid formation of cracks in diamond coating and extensive plastic deformation of titanium substrate, (2) debonding and/or penetration of the cracks into the film, and (3) removal or delamination of the films from the substrate. Transgranular fracture is common with CVD diamond films impacted by sand particles as shown in Fig. 14(e).

3.2.2 Laser-Treated Titanium. The erosion mass losses of laser-treated Ti are plotted in Fig. 11(a) and (b). Compared with untreated Ti substrate, the erosion resistance of a laser-treated specimen is much higher under both low and high impact velocities (Fig. 11). There is a significant difference in the material removal mechanisms between the untreated and laser-nitrided Ti samples. Titanium samples, being more ductile, show extensive plastic deformation and ploughing, whereas, the typical features of erosion failure of laser-alloyed specimen are the indentation-like impact craters and the appearance of cracks emitting from these impact craters (Fig. 15a). The formation of these cracks can be related to high hardness and low ductility of the laser-nitrided layer as well as the presence of tensile stresses, which increase the crack sensitivities of nitrided layers. Emanating radial cracks form, grow gradually, and intersect with each other, eventually causing chipping and material removal by brittle fracture, as shown in Fig. 15(b).

4. Discussion

The erosion rate of brittle materials or hard coatings can be described using the following equation:[26]

$$e \propto E^{a}/H^{b}K_{IC}^{c}$$

where E is the modulus of elasticity; H is the hardness; K_{IC} is the fracture toughness; and a, b, and c are constants. According to this equation, to minimize the erosion rate, a combination of high hardness and high fracture toughness is required. Furthermore, fine grain size, high adhesion strength (or load-bearing capacity), and enough hardening depth are essential for good erosion resistance of surface coatings or treatments.[27]

Erosion resistance is closely related to the nature of the deposited coating as well as the interfacial structure between the coating and the substrate (adhesion, load-bearing capacity, *etc.*). Carbon nitride thin films exhibit a unique combination of properties: extreme hardness, chemical inertness, and excellent tribological behavior; however, adhesion problems and high residual stress limit the thickness of the coating. For duplex-treated coating, microcracks easily propagate through the interface between CN_X film and plasma-nitrided layers. Although this crack deflection mechanism improves the impact resistance until the rupture of the coating, it is only effective under a low impact velocity of erodents. Under a high impact velocity, the spallation of the CN_X layer is more significant and the hardening depth of laser-treated Ti is quite shallow; thus, the erosion resistance is poor.

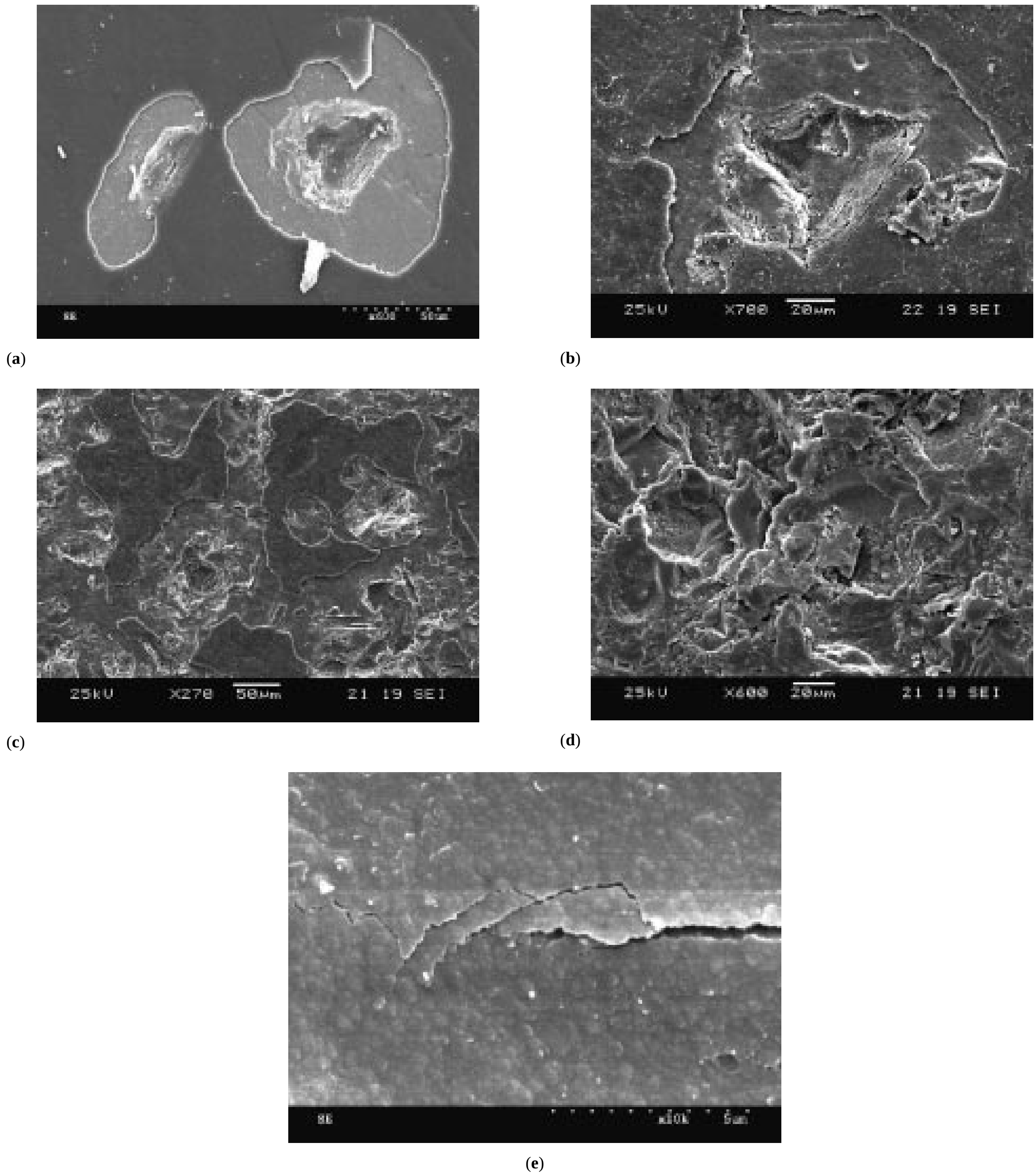


Fig. 14 (**a**) through (**e**) Erosion morphologies of diamond-coated titanium substrate

The use of diamond coating in erosion situations looks attractive because of its high hardness and good wear resistance, but the application is often limited by low adhesion or load-bearing capacity, as determined by the indentation tests. In erosion tests, it is generally observed that the coating peels off or delaminates rather than showing the erosion wear. The major problem with CVD diamond coating is associated with stresses, that is, the intrinsic stresses and thermal stresses, acting to cause the coating to delaminate. Thin diamond film (less than 3 μm) can have a better adhesion with substrate but is insufficient to withstand the sand particle impact. With an increase in the coating thickness, the residual stress will increase. Coatings with residual

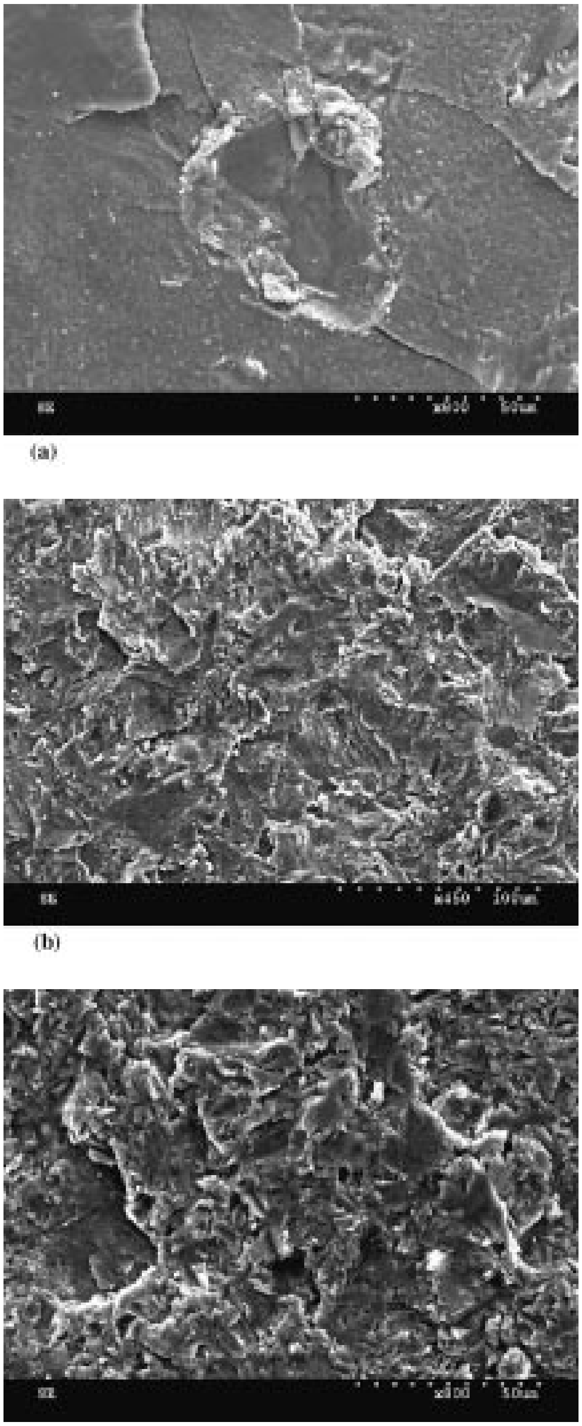


Fig. 15 (**a**) through (**c**) Erosion morphology of laser-nitrided titanium substrate

stresses high enough to cause debonding from the substrate will be detrimental to the performance. However, there are a few reports indicating that when the coating thickness exceeds 10 to 20 μm, the measured residual stresses gradually decrease with the coating thickness.[28] Also, by increasing the coating thickness, the distance between the impact particles and the weak substrate can be increased, and the impact influence can be constrained within the coating or away from the interface, thus improving the erosion resistance. Some researchers have prepared very thick diamond coating (35 or 100 μm), which is quite effective in preventing erosion resistance.[28,29] To prepare very thick diamond coating, microwave and hot-filament chemical vapor deposition are probably not potential industrial techniques because of their low deposition rate. The potential techniques probably include d.c. plasma jet CVD processes (with which the diamond can be deposited at a high growth rate up to 1 mm/h) and d.c. PACVD methods (with a high growth rate comparable to d.c. plasma jet CVD, but an order of magnitude smaller gas consumption).[29]

In this study, laser alloying the Ti substrate shows the best erosion resistance. This is easily understood since (1) the hardening depth is quite large (around 200 μm); and (2) there is no problem with spallation or poor adhesion. Compared with the other two methods applied in this study, laser surface alloying is quite efficient (the processing time is just a few minutes) and convenient (no need for a vacuum condition). If the residual stresses and the defects, such as cracking, porosity, *etc.*, in the laser-treated layer, can be controlled precisely, then laser surface alloying is probably one of the viable methods for improving the erosion resistance of Ti and its alloys.

5. Conclusions

To improve the erosion resistance of pure titanium, different surface treatment methods were applied. The following results were obtained from this study.

- Duplex-treated coating with CN_X films deposited on a plasma-nitrided layer can improve the erosion resistance of titanium substrate under a low impact velocity. However, under high velocity, due to the shallow hardening depth of plasma nitriding, the improvement of erosion resistance is not so significant.
- Diamond coatings showed a low erosion resistance due to the large-area spallation during erosion, which can be attributed to the high residual stresses and poor adhesion strength in the coatings.
- Compared with untreated Ti substrate, the erosion resistance of a laser-treated specimen has been improved significantly.

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